Effects of arbitrarily directed field on spin phase oscillations in biaxial molecular magnets

Hui Hu*

Department of Physics, Tsinghua University, Beijing 100084, P. R. China

Jia-Lin Zhu

Department of Physics, Tsinghua University, Beijing 100084, P. R. China

Center for Advanced Study, Tsinghua University, Beijing 100084, P. R. China

Rong Lü

Center for Advanced Study, Tsinghua University, Beijing 100084, P. R. China

Jia-Jiong Xiong

Department of Physics, Tsinghua University, Beijing 100084, P. R. China

Abstract

Quantum phase interference and spin-parity effects are studied in biaxial molecular magnets in a magnetic field at an arbitrarily directed angle. The calculations of the ground-state tunnel splitting are performed on the basis of the instanton technique in the spin-coherent-state path-integral representation, and complemented by exactly numerical diagonalization. Both the Wentzel-Kramers-Brillouin exponent and the preexponential factor are obtained for the entire region of the direction of the field. Our results show that the tunnel splitting oscillates with the field for the small field angle, while for

*To whom the correspondence should be addressed.

Email: huhui@Phys.Tsinghua.edu.cn

the large field angle the oscillation is completely suppressed. This distinct angular dependence, together with the dependence of the tunnel splitting on the field strengh, provide an independent test for spin-parity effects in biaxial molecular magnets. The analytical results for the molecular Fe_8 magnet, are found to be in good areement with the numerical simulations, which suggests that even the molecular magnet with total spin $S = 10$ is large enough to be treated as a giant spin system.

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I. INTRODUCTION

In recent years, owing mainly to the rapid advances both in new technologies of miniaturization and in highly sensitive SQUID magnetometry, there have been considerable theoretical and experimental studies carried out on the nanometer-scale magnets which exhibit macroscopic quantum phenomena(MQP).[1] A number of nanometer-scale particles in the superparamagnetic regime have been identified as candidates for the observation of MQP such as the tunneling of the magnetization (or the Néel vector) out of metastable potential minimum through the classically impenetrable barrier to a stable one, i.e., macroscopic quantum tunneling (MQT), or, more strikingly, macroscopic quantum coherence (MQC), where the magnetization (or the Néel vector) coherently oscillates between energetically degenerate easy directions over many periods. Up to now, molecular magnets have been the most promising candidates to observe MQP because they have well-defined structures and magnetic properties. The system that have recently attracted much attention are the molecules $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ (in short $Mn_{12}Ac$)[2] and $[(tacn)_6Fe_8O_2(OH)_{12}]^{8+}$ (in short Fe_8),[3] where tacn is a macrocyclic ligand triazacyclononance. The $Mn_{12}Ac$ molecule contains four Mn^{4+} ($S = 3/2$) ions in a central tretrahedron surrounded by eight Mn^{3+} ($S = 2$) ions. Oxygen bridges allow superexchange coupling among the Mn ions, and both high-field and ac susceptometry experiments indicate a $S = 10$ ground state, resulting from the four inner Mn^{4+} spins being paralleled to each other and the other eight Mn^{3+} also parallel with the two groups antiparallel to each other. The magnetization relaxation experiments, the dynamic susceptibility measurements, and the dynamic hysteresis experiments all indicate that the thermally assisted, magnetic-field-tuned resonant coherently quantum tunneling of magnetization occurs between spin states in a large number of identical $Mn_{12}Ac$ molecules.[2] Magnetic measurements have shown that Fe_8 also has a spin ground state $S = 10$, which arises from competing antiferromagnetic interactions between the eight $S = 5/2$ iron spins with six spins being parallel and antiparallel to the other two spins.[3]

One of the most striking effects in the magnetic MQP is that for some spin systems

with high symmetries, the tunneling behaviors of magnetization seem sensitive to the parity of total spin of the magnet. It has been theoretically demonstrated[4,5] that the ground-state tunneling level splitting is completely suppressed to zero for the half-integer total spin ferromagnets with biaxial crystal symmetry in the absence of an external magnetic field, resulting from the destructive interference of the Berry phase or the Wess-Zumino, Chern-Simons term in the Euclidean action between the symmetry-related tunneling paths connecting two classically degenerate minima. Such destructive interference effect for half-integer spins is known as the topological quenching.[6] But for the integer spins, the quantum interference between topologically different tunneling paths is constructive, and therefore the ground-state tunneling level splitting is nonzero. While such spin-parity effects are sometimes related to Kramers degeneracy, they typically go beyond this theorem in rather unexpected ways.[4,6–8] One recent experimental method based on the Landau-Zener model was developed by Wernsdorfer and Sessoli[9] to measure the very small tunnel splitting on the order of 10^{-8}K in molecular Fe_8 magnets. They observed a clear oscillation of the tunnel splitting as a function of the magnetic field applied along the hard anisotropy axis, which is direct evidence of the role of the topological spin phase (Berry phase) in the spin dynamics of these molecules.

Motivated by the experiment on topological phase interference or spin-parity effects in the molecule Fe_8,[9] in this paper we investigate the resonant quantum tunneling of the magnetization vector in molecular magnets with biaxial crystal symmetry in the presence of an external magnetic field at an arbitrarily directed angle in the ZY plane. By applying the instanton technique in the spin-coherent-state path-integral representation,[10] we calculate both the Wentzel-Kramers-Brillouin (WKB) exponent and the preexponential factor in the ground-state tunnel splitting. Our results show that for the small angle θ_H of the applied magnetic field, the ground-state tunnel splitting oscillates with the field for both the integer and half-integer spins, and the oscillation behavior for integer spins is significantly different from that for half-integer spins. However, this oscillation is completely suppressed for the large angle region. The distinct angular dependence, together with the dependence of the

ground-state tunnel splitting on the strength of the external applied magnetic field, may provide an independent experimental test for spin-parity effects in molecular magnets. It is noted that the instanton technique is semiclassical in nature, i.e., valid for large spins and in the continuum limit. Whether the instanton technique can be applied in studying the spin dynamics in the molecular magnet with $S = 10$ (such as Fe_8) is an open question. We study this problem with the help of exact diagonalization calculation. Our results show that the analytical calculation based on the instanton technique agrees excellently well with the exact diagonalization calculation, which strongly suggests that the molecular magnet with $S = 10$ can be treated as a giant spin system.

II. MODEL AND METHOD

The system of interest is a molecular magnet at a temperature well below its anisotropy gap, which has the following Euclidean action in the spin-coherent-state representation,[10]

$$S_E(\theta, \phi) = \int d\tau \left[iS \left(\frac{d\phi}{d\tau} \right) - iS \left(\frac{d\phi}{d\tau} \right) \cos\theta + E(\theta, \phi) \right], \tag{1}$$

where S is the total spin of the molecular magnet. The polar angle θ and the azimuthal angle ϕ label the spin coherent state. $E(\theta, \phi)$ is the total energy of the molecular magnet which includes the magnetocrystalline anisotropy energy and the Zeeman energy when an external magnetic field is applied.

It is noted that the Euclidean action is written in the north-pole gauge, and the first two terms in Eq. (1) define the Wess-Zumino or Berry term which arises from the nonorthogonality of spin coherent states. The Wess-Zumino term has a simple geometrical or topological interpretation. For a closed path, this term equals $-iS$ times the area swept out on the unit sphere between the path and the north pole. The first term in Eq. (1) is a total imaginary-time derivative, which has no effect on the classical equation of motion for the magnetization vector, but yields the boundary contribution to the Euclidean action. Loss et al.[4] and von Delft and Henley[5] studied the physical effect of this total derivative term,

and they found that this term is crucial for the quantum properties of the magnetic particle and makes the tunneling behaviors of integer and half-integer spins strikingly different.

In the semiclassical limit, the dominant contribution to the Euclidean transition amplitude comes from finite action solutions of the classical equations of motion (instantons), which can be expressed as the following equations in the spherical coordinate system,[10]

$$iS\left(\frac{d\overline{\theta}}{d\tau}\right)\sin\overline{\theta}=\frac{\partial E}{\partial\overline{\phi}}, \tag{2}$$

$$iS\left(\frac{d\overline{\phi}}{d\tau}\right)\sin\overline{\theta}=-\frac{\partial E}{\partial\overline{\theta}}, \tag{3}$$

where $\overline{\theta}$ and $\overline{\phi}$ denote the classical path. Note that the Euclidean action Eq. (1) describes the $(1\oplus 1)-$dimensional dynamics in the Hamiltonian formulation with canonical variables ϕ and $P_\phi = S(1-\cos\theta)$.

According to the instanton technique in the spin-coherent-state path-integral representation, the instanton's contribution to the tunneling rate Γ for MQT or the ground-state tunnel splitting Δ for MQC (not including the geometric phase factor generated by the topological term in the Euclidean action) is given by[10]

$$\Gamma\ (or\ \Delta)=p_0\omega_p\left(\frac{S_{cl}}{2\pi}\right)^{1/2}e^{-S_{cl}}, \tag{4}$$

where ω_p is the small-angle precession or oscillation frequency in the well, and S_{cl} is the classical action or the WKB exponent which minimizes the Euclidean action of Eq. (1). The preexponential factor p_0 originates from the quantum fluctuations about the classical path, which can be evaluated by expanding the Euclidean action to second order in the small fluctuations.

We describe the molecular magnet with biaxial crystal symmetry by the standard Hamiltonian,[6]

$$\mathcal{H}=k_1\hat{S}_z^2+k_2\hat{S}_y^2, \tag{5}$$

where $k_1 > k_2 > 0$ are proportional to the anisotropy coefficients, and we take the easy, medium, and hard axes as **x**, **y**, and **z**, respectively. If the magnetic field is applied in ZY plane, at an arbitrary angle $0\leqslant\theta_H\leqslant 90^o$ with **z**, the Hamiltonian becomes[7,9]

$$\mathcal{H} = k_1\hat{S}_z^2 + k_2\hat{S}_y^2 - g\mu_B H_z\hat{S}_z - g\mu_B H_y\hat{S}_y, \tag{6}$$

where g is the landé factor, and μ_B is the Bohr magneton. The Zeeman energy term associated with the applied field $\vec{H} \equiv (0, H_y, H_z) \equiv (0, H\sin\theta_H, H\cos\theta_H)$ is given in the last two terms of the Hamiltonian. If the field is below some critical value $H_c(\theta_H)$ (to be computed), the Hamiltonian Eq. (6) has two degenerate minima, and therefore the magnetization can resonate between these two directions, providing a case of MQC. Under the spin-coherent-state and the imaginary time representation, the $E(\theta,\phi)$ term in the Euclidean action is given by

$$\begin{aligned} E(\theta,\phi) &= k_1S^2\cos^2\theta + k_2S^2\sin^2\theta\sin^2\phi - g\mu_B SH_z\cos\theta - g\mu_B SH_y\sin\theta\sin\phi \\ &= K_1\cos^2\theta + K_2\sin^2\theta\sin^2\phi - 2K_1(H_z/H_a)\cos\theta - 2K_1(H_y/H_a)\sin\theta\sin\phi, \end{aligned} \tag{7}$$

with $K_1 = k_1S^2$ and $K_2 = k_2S^2$ being the transverse and longitudinal anisotropy coefficients respectively, and $H_a = 2K_1/g\mu_B S$ being the anisotropy field. Introducing $\lambda = K_2/K_1$, $\cos\theta_0 = H\cos\theta_H/H_a$, and $\sin\theta_0\sin\phi_0 = H\sin\theta_H/\lambda H_a$, the $E(\theta,\phi)$ reduces to

$$E(\theta,\phi) = K_1(\cos\theta - \cos\theta_0)^2 + K_2(\sin\theta\sin\phi - \sin\theta_0\sin\phi_0)^2 + E_0, \tag{8}$$

where E_0 is a constant that makes $E(\theta,\phi)$ zero at the initial state. It is clearly shown in Eq. (8) that the energy minima of system are at $\theta_1 = \theta_0$, $\phi_1 = \phi_0$ and $\theta_2 = \theta_0$, $\phi_2 = \pi - \phi_0$, and therefore there are two different instanton paths of opposite windings around hard anisotropy axis. We denote them by instanton $A: \phi = \phi_0 \longrightarrow \phi = +\pi/2 \longrightarrow \phi = \pi - \phi_0$, and instanton $B: \phi = \phi_0 \longrightarrow \phi = -\pi/2 \longrightarrow \phi = \pi - \phi_0$.

The critical field at which the energy barrier disappears can be determined by,

$$\cos\theta_0 = \frac{H\cos\theta_H}{H_a} \leqslant 1, \tag{9}$$

$$\sin\phi_0 = \frac{H\sin\theta_H}{\lambda H_a\left(1 - \frac{H^2\cos^2\theta_H}{H_a^2}\right)^{1/2}} \leqslant 1. \tag{10}$$

Taking into account Eqs. (9) and (10), we obtain

$$H_c = \frac{\lambda H_a}{\left(\sin^2\theta_H + \lambda^2\cos^2\theta_H\right)^{1/2}}. \tag{11}$$

For the special cases $\theta_H = 0,\ \pi/2$, we have $H_c = H_a,\ \lambda H_a$, respectively. The dependence of H_c/H_a on θ_H is plotted in Fig. 1 for $\lambda = 0.71$.

Now we investigate the tunneling behaviors of magnetization by applying the instanton technique in the spin-coherent-state path-integral representation. First of all, we must find out the classical path $\bar{\theta}$ and $\bar{\phi}$ that satisfies the boundary condition. Along the classical path, $E(\bar{\theta}, \bar{\phi})$ is conserved, so that the relation between $\bar{\theta}(\tau)$ and $\bar{\phi}(\tau)$ can be found purely by using energy conservation.[6,7] After some algebra, we obtain

$$\cos\bar{\theta} = \frac{\left(\cos\theta_0 - \lambda^{1/2} y \sin\bar{\phi}\right) \pm i\lambda^{1/2}\left(x\sin\bar{\phi} - \sin\theta_0\sin\phi_0\right)}{1 - \lambda\sin^2\bar{\phi}}, \tag{12}$$

where x, y are variables defined by

$$x = \left\{\frac{(a^2+b^2)^{1/2} + a}{2}\right\}^{1/2} \qquad \text{and} \qquad y = \left\{\frac{(a^2+b^2)^{1/2} - a}{2}\right\}^{1/2}, \tag{13}$$

with $a = 1 - \cos^2\theta_0 - \lambda\sin^2\bar{\phi} + \lambda\sin^2\theta_0\sin^2\phi_0$ and $b = 2\lambda^{1/2}\sin\theta_0\cos\theta_0\sin\phi_0$. Here we assume that the condition $a \geqslant 0$ is always fulfilled for the small magnetic field H. The positive and negative sign in Eq. (12) are corresponding to instanton and anti-instanton solutions for path A or B, respectively. For the low magnetic field , one can take $\bar{\phi}(\tau)$ to be entirely real (see appendix A for detail).[6] Then through the expression $S_{cl} = iS\int_{-\infty}^{+\infty}(1 - \cos(\bar{\theta}))(d\bar{\phi}/d\tau)d\tau$, the desired Wentzel-Kramers-Brillouin (WKB) exponents (or classical actions) are found to be

$$\begin{aligned}\mathrm{Im}(S_{cl}^A) &= S(+\pi - 2\phi_0) - \frac{2S\cos\theta_0}{(1-\lambda)^{1/2}}\left(\frac{\pi}{2} - \arctan\left((1-\lambda)^{1/2}\tan\phi_0\right)\right) \\ &\quad + 2\lambda^{1/2} S\int_{\phi_0}^{\pi/2}\frac{y\sin\phi d\phi}{1-\lambda\sin^2\phi},\end{aligned}$$

$$\begin{aligned}\mathrm{Re}(S_{cl}^A) &= 2\lambda^{1/2} S\left\{\frac{\sin\theta_0\sin\phi_0}{(1-\lambda)^{1/2}}\left(-\frac{\pi}{2} + \arctan\left((1-\lambda)^{1/2}\tan\phi_0\right)\right)\right. \\ &\quad \left. + \int_{\phi_0}^{\pi/2}\frac{x\sin\phi d\phi}{1-\lambda\sin^2\phi}\right\}\end{aligned} \tag{14}$$

for instanton A, and

$$\mathrm{Im}(S_{cl}^B) = S(-\pi - 2\phi_0) + \frac{2S\cos\theta_0}{(1-\lambda)^{1/2}}\left(\frac{\pi}{2} + \arctan\left((1-\lambda)^{1/2}\tan\phi_0\right)\right)$$
$$+2\lambda^{1/2}S\int_{\phi_0}^{\pi/2}\frac{y\sin\phi d\phi}{1-\lambda\sin^2\phi},$$

$$\mathrm{Re}(S_{cl}^B) = 2\lambda^{1/2}S\left\{\frac{\sin\theta_0\sin\phi_0}{(1-\lambda)^{1/2}}\left(+\frac{\pi}{2} + \arctan\left((1-\lambda)^{1/2}\tan\phi_0\right)\right)\right.$$
$$\left. + \int_{\phi_0}^{\pi/2}\frac{x\sin\phi d\phi}{1-\lambda\sin^2\phi}\right\} \tag{15}$$

for instanton B. Therefore, the difference of the action of two tunneling paths is

$$\mathrm{Im}(\Delta S_{cl}) = \mathrm{Im}(S_{cl}^B) - \mathrm{Im}(S_{cl}^A) = -2S\pi\left(1 - \frac{\cos\theta_0}{(1-\lambda)^{1/2}}\right) \equiv -2\Phi(H), \tag{16}$$

$$\mathrm{Re}(\Delta S_{cl}) = \mathrm{Re}(S_{cl}^B) - \mathrm{Re}(S_{cl}^A) = 2S\pi\sin\theta_0\sin\phi_0\left(\frac{\lambda}{1-\lambda}\right)^{1/2}. \tag{17}$$

Note that $\mathrm{Im}(\Delta S_{cl})$ comes from the Berry phase $iS(1-\cos\bar{\theta})\left(d\bar{\phi}/d\tau\right)$, and leads to the oscillation of the ground-state tunnel splitting with the magnetic field.

The preexponential factor in the tunnel splitting can be evaluated by taking the asymptotic form of zero-mode $\left(d\overline{\phi}/d\tau\right)$,[10] which can be deduced from the classical equations of motion (see appendix A).

Finally, the ground-state tunnel splitting is found to be

$$\hbar\Delta = \hbar\Delta_0\left|1 + e^{2i\Phi(H)}e^{-\mathrm{Re}\,\Delta S_{cl}}\right|$$
$$= \hbar\Delta_0\left\{\left(1 - e^{-\mathrm{Re}\,\Delta S_{cl}}\right)^2 + 4e^{-\mathrm{Re}\,\Delta S_{cl}}\cos^2\Phi(H)\right\}^{1/2}, \tag{18}$$

with

$$\hbar\Delta_0 = c\omega_0^{3/2}\frac{4\sin\theta_0}{\left(\sin^2\theta_0 - \lambda\right)^{1/2}}\left(\frac{S^2}{2\pi K_1}\right)^{1/2}\left(\frac{\sin^2\theta_0}{\sin^2\theta_0 + \lambda\cos^2\theta_0\sin^2\phi_0}\right)^{1/2}e^{-\mathrm{Re}(S_{cl}^A)}, \tag{19}$$

where $\omega_0 = (2K_1/S)\lambda^{1/2}\sin\theta_0\cos\phi_0$. The dimensionless prefactor c can often be of order 1 or so, and is therefore relevant to the exact diagonalization calculation.

III. RESULTS AND DISCUSSION

Before we discuss the Eq. (18), we note here that our model can be directly related to the model describing the molecular Fe_8 magnet,[9]

$$\mathcal{H} = -D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + g\mu_B H_x' \hat{S}_x + g\mu_B H_y' \hat{S}_y, \tag{20}$$

with $K_1 = (D+E)S^2$, $K_2 = (D-E)S^2$ and $H_z = H_x'$, $H_y = -H_y'$. According to the typical parameters of Fe_8, $D = 0.275$K, $E = 0.046$K and $g = 2$, we obtain that $K_1 = 32.1$K, $K_2 = 22.9$K, $\lambda = 0.71$ and $H_a = 4.77$T. These parameters are used throughout the whole calculation.

First, we discuss the effects of arbitrarily directed field on the spin phase oscillation. Our results show that the topological phase interference or spin-parity effects depend on the direction of the magnetic field significantly. From Eq (18), whether the ground-state tunnel splitting oscillates with the field is determined by two factors, $\Phi(H)$ and $\mathrm{Re}(\Delta S_{cl})$. For a fixed field strength, i.e. $H \equiv H_S \equiv \left(\sqrt{H_y^2 + H_z^2}\right)$, it brings two-fold effects to increase the field angle θ_H: (i) the dependence of $\Phi(H)$ on the field strength is reduced. As θ_H increases up to $\frac{\pi}{2}$, $\Phi(H) \equiv \pi S \left(1 - \frac{H\cos\theta_H}{(1-\lambda)^{1/2} H_a}\right)$ gradually reduces to a constant πS. (ii) The degree of oscillation σ which is defined as a ratio of the oscillation part $4e^{-\mathrm{Re}\,\Delta S_{cl}}$ to the non-oscillation part $\left(1 - e^{-\mathrm{Re}\,\Delta S_{cl}}\right)^2$ in Eq. (18) decreases from $+\infty$ to a small value.

For $\theta_H = 0$ (the field is along the hard anisotropy axis), the symmetry of two classical paths imposes $\mathrm{Re}(\Delta S_{cl}) = 0$, then, the tunnel splitting $\Delta = 2\Delta_0 \left|\cos\Phi(H)\right|$ oscillates with the field and thus vanish whenever

$$\frac{H}{H_a} = (1-\lambda)^{1/2} \frac{(S - n - 1/2)}{S}, \tag{21}$$

where $n = 0, 1, 2, ...$ is an integer.[6] For $\theta_H = \frac{\pi}{2}$ (the field is along the medium anisotropy axis), on the other hand, $\Phi(H)$ becomes a constant πS, and therefore the tunnel splitting increases monotonically with the field. When the field is applied in ZY plane with an arbitrarily angle θ_H, one may expect to observe a crossover for a certain field angle θ_H^c.

Choosing the magnitude of $\vec{H}$ to be the first value that makes $\cos\Phi(H) = 0$ and taking $\sigma = 1$, we obtain

$$\theta_H^c \approx \arctan\left(\frac{1.76\lambda^{1/2}}{\pi}\right) \tag{22}$$

For the molecular Fe_8 magnet, $\lambda = 0.71$, we find $\theta_H^c \approx 25^o$, which agrees well with the exact diagonalization calculation (shown in Fig. 2a) and the experimental results obtained by Wernsdorfer and Sessoli.[9] It is noted that the value of θ_H^c is independent of the total spin S of the molecular magnet, and depends on the parameter λ only. For highly anisotropic materials, the typical values of the transverse and longitudinal anisotropy coefficients are $K_1 \approx 10^7 \mathrm{erg/cm}^3$ and $K_2 \approx 10^5 \mathrm{erg/cm}^3$. Thus, $\lambda = 0.01$, the value of θ_H^c is estimated to be 3.2^o and is much smaller than that for the molecular Fe_8 magnet, which means that even a very small misalignment of the field with the hard anisotropy axis can completely destroy the oscillation. Therefore, the molecular Fe_8 magnet is a better candidate for observing the oscillation of the ground-state tunnel splitting with the field compared with the highly anisotropic materials.

Next, we turn to the comparison between the analytical calculations and the numerical stimulations. It is noted that the instanton approach is semiclassical in nature, i.e., valid for large spins and in the continuum limit. Whether the instanton technique can be applied in studying the spin dynamics in molecular magnets with $S = 10$ (such as Fe_8) is an open question. We have performed the numerical diagonalization of the Hamiltonian Eq. (6) for the molecular Fe_8 magnet in the presence of an external magnetic field at an arbitrarily directed angle in ZY plane. As illustrated in Fig. 2a, for Fe_8, the analytical results based on the instanton technique are in good agreement with the exact diagonalization results. In order to show the agreement more clearly, we have presented the numerical and analytical results in Table 1 for the molecular Fe_8 magnet in the magnetic field applied at angle $\theta_H = 0^o$, 15^o, 30^o and 90^o. It is clearly shown that the accuracy of the semiclassical calculation is very high for the low magnetic field up to $H = 1.0\mathrm{T}$ for the entire region of the angle $0^o \leqslant \theta_H \leqslant 90^o$. As a result, we conclude that the molecular magnet with

$S = 10$ can be treated as a giant spin system. The numerical and analytical calculated tunnel splitting as a function of the field are shown in Fig. 2b for half-integer spin $S = 9.5$, and the good agreement between numerical and analytical results is also found. From Fig. 2, it is obviously that the tunneling behavior of magnetization of integer spins is significantly different from that for half-integer spins. At the end of this section, we present the results with different parameter λ for the field along $\mathbf{z}$ or $\mathbf{y}$ in Figs. (3a) and (3b). It is interesting to note that the tunnel splitting increases rapidly by lowing the parameter λ, which suggests that highly anisotropic materials are more suitable for observing MQP in experiments.

In conclusion, we have studied the ground-state tunnel splitting in the molecular magnets with biaxial crystal symmetry in the presence of an external magnetic field at an arbitrarily directed angle. The switching from oscillation to the monotonic growth of the ground-state tunnel splitting on the field angle has been shown in detail. Our results are suitable for a quantitative description of some aspects of the new experimental behavior on the molecular Fe_8 magnets.[9]

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Appendix A: Evaluate the ground-state tunnel splitting

In this appendix, the general scheme for calculation of the ground-state tunnel splitting is presented, the main assumptions and approximations are also outlined.

We start with the relation between $\theta(\tau)$ and $\phi(\tau)$ obtained from the energy conversion[6] (see Eq. (12)). Only one instanton, say the + one, need be considered explicitly (from now on, we drop all the bars and identify $\theta = \bar{\theta}(\tau)$, $\phi = \bar{\phi}(\tau)$ for convenient):

$$\cos\theta = \frac{\left(\cos\theta_0 - \lambda^{1/2} y \sin\phi\right) + i\lambda^{1/2}\left(x \sin\phi - \sin\theta_0 \sin\phi_0\right)}{1 - \lambda \sin^2\phi}, \tag{23}$$

$$\sin\theta = \frac{(x - \lambda\sin\theta_0\sin\phi_0\sin\phi) - i\left(\lambda^{1/2}\cos\theta_0\sin\phi - y\right)}{1-\lambda\sin^2\phi}. \tag{24}$$

In order to determine the classical paths, we need another equation of motion(see Eq. (3)),

$$\begin{aligned} iS\sin\theta\dot{\phi} &= -\frac{\partial E(\theta,\phi)}{\partial\theta} \\ &= 2K_1(\cos\theta - \cos\theta_0)\sin\theta - 2K_2(\sin\theta\sin\phi - \sin\theta_0\sin\phi_0)\cos\theta\sin\phi. \end{aligned} \tag{25}$$

After dividing the factor $2K_1\sin\theta$ on both sides and substituting Eqs. (23) and (24), we rewrite Eq. (25) as

$$\begin{aligned} i\frac{S}{2K_1}\dot{\phi} &= -\lambda^{1/2}y\sin\phi + i\lambda^{1/2}\left(x\sin\phi - \sin\theta_0\sin\phi_0\right) + \\ &\quad \lambda\sin\theta_0\sin\phi_0\sin\phi\frac{\left(\cos\theta_0 - \lambda^{1/2}y\sin\phi\right) + i\lambda^{1/2}\left(x\sin\phi - \sin\theta_0\sin\phi_0\right)}{(x-\lambda\sin\theta_0\sin\phi_0\sin\phi) - i\left(\lambda^{1/2}\cos\theta_0\sin\phi - y\right)} \\ &= \operatorname{Re} f(\phi) + i\operatorname{Im} f(\phi), \end{aligned} \tag{26}$$

where

$$\begin{aligned} \operatorname{Re} f(\phi) &= -\lambda^{1/2}y\sin\phi + \lambda\sin\theta_0\sin\phi_0\sin\phi \\ &\quad \times\frac{\left(1-\lambda\sin^2\phi\right)\left(x\cos\theta_0 - \lambda^{1/2}\sin\theta_0\sin\phi_0\right)}{(x-\lambda\sin\theta_0\sin\phi_0\sin\phi)^2 + \left(\lambda^{1/2}\cos\theta_0\sin\phi - y\right)^2}, \end{aligned} \tag{27}$$

$$\begin{aligned} \operatorname{Im} f(\phi) &= \lambda^{1/2}\left(x\sin\phi - \sin\theta_0\sin\phi_0\right) + \lambda\sin\theta_0\sin\phi_0\sin\phi \\ &\quad \left[\left(\cos\theta_0 - \lambda^{1/2}y\sin\phi\right)\left(\lambda^{1/2}\cos\theta_0\sin\phi - y\right) + \lambda^{1/2}\times\right. \\ &\quad \times\frac{\left.(x\sin\phi - \sin\theta_0\sin\phi_0)\,(x-\lambda\sin\theta_0\sin\phi_0\sin\phi)\right]}{(x-\lambda\sin\theta_0\sin\phi_0\sin\phi)^2 + \left(\lambda^{1/2}\cos\theta_0\sin\phi - y\right)^2}. \end{aligned} \tag{28}$$

As shown in Eq. (26) , if $\operatorname{Re} f(\phi\ )$ is always zero for arbitrary ϕ, one can then take $\phi(\tau)$ to be entirely real. Unfortunately, it is not the case, $\operatorname{Re} f(\phi\ )$ is not always zero *except* $H_z = 0$ or $H_y = 0$. Checking the right-hand-side of Eq. (27) more carefully, we find that up to the leading term, Eq. (27) can be rewritten as

$$|\operatorname{Re} f(\phi)| \approx \frac{\lambda^2\sin^3\phi}{\left(1-\lambda\sin^2\phi\right)^{1/2}}\cos\theta_0\sin\phi_0$$

$$
\begin{aligned}
&\leqslant \frac{\lambda^2}{(1-\lambda)^{1/2}}\cos\theta_0\sin\phi_0 \\
&\approx \frac{\lambda}{(1-\lambda)^{1/2}}\frac{H_z H_y}{H_a^2} \\
&= \frac{\lambda}{2\,(1-\lambda)^{1/2}}\frac{H^2\sin 2\theta_H}{H_a^2}.
\end{aligned}
\tag{29}
$$

It is clearly shown from Eq. (29) that the $\operatorname{Re} f(\phi)$ is almost two orders of magnitude smaller than $\operatorname{Im} f(\phi)$ for the low magnetic field(i.e., for $H/H_a \leqslant 1/5$). So it is sufficient to drop the term $\operatorname{Re} f(\phi)$ in Eq. (26) for the first order approximation and treat $\phi(\tau)$ as a real variable. Under this assumption, the classical Euclidean action can be evaluated easily without resolving the analytical solutions of $\theta(\tau)$ and $\phi(\tau)$,

$$
\begin{aligned}
S_{cl} &= iS\int_{-\infty}^{+\infty}(1-\cos(\theta(\tau)))(d\phi/d\tau)d\tau \\
&= iS\int_{\phi_i}^{\phi_f}(1-\cos(\theta(\phi)))d\phi \\
&= iS\int_{\phi_i}^{\phi_f}\left(1-\frac{\left(\cos\theta_0-\lambda^{1/2}y\sin\phi\right)+i\lambda^{1/2}\left(x\sin\phi-\sin\theta_0\sin\phi_0\right)}{1-\lambda\sin^2\phi}\right)d\phi,
\end{aligned}
\tag{30}
$$

where $\phi_i = \phi(\tau\to-\infty)$, $\phi_f = \phi(\tau\to+\infty)$. The results for instantons A and B are given in Eqs. (14) and (15).

Next let us study the preexponential factor at two different magnetic field directions of $\theta_H = 0$ and $\pi/2 \geqslant \theta_H > 0$.

I. $\theta_H = 0$

The preexponential factor can be evaluated from zero-mode $(d\phi/d\tau)$.[10] It is obvious from symmetry that the preexponential factors along two instanton path A and B are equal.

For $\theta_H = 0$, we have $\phi_0 = 0$ and $\phi_i = 0$, $\phi_f = \pi$. Then, from Eq. (13) we get $x = \left(1-\cos^2\theta_0-\lambda\sin^2\phi\right)^{1/2}$ and $y = 0$. Therefore, Eq. (26) reduces to

$$
\dot{\phi} = \frac{2K_1}{S}\lambda^{1/2}\left(1-\cos^2\theta_0-\lambda\sin^2\phi\right)^{1/2}\sin\phi. \tag{31}
$$

This equation can be integrated easily. Defining $\omega_0 = \frac{2K_1}{S}\lambda^{1/2}\sin\theta_0$, we obtain

$$\cos\phi = \left(1-\cos^2\theta_0-\lambda\right)^{1/2} \frac{\tanh(\omega_0\tau)}{\left(1-\cos^2\theta_0-\lambda\tanh^2\left(\omega_0\tau\right)\right)^{1/2}}. \tag{32}$$

It is easily verified that $\phi \to 0, \pi$, as $\tau \to \pm\infty$.

Following the standard procedure of the Ref. 10, we write the final result as

$$\hbar\Delta = c\omega_0^{3/2} \frac{8\sin\theta_0}{\left(1-\cos^2\theta_0-\lambda\right)^{1/2}} \left(\frac{S^2}{2\pi K_1}\right)^{1/2} e^{-S_{cl}} \left|\cos\Phi(H)\right|, \tag{33}$$

where

$$S_{cl} = 2S\left\{\frac{1}{2}\ln\left(\frac{1+\frac{\lambda^{1/2}}{\sin\theta_0}}{1-\frac{\lambda^{1/2}}{\sin\theta_0}}\right) - \frac{\cos\theta_0}{2\left(1-\lambda\right)^{1/2}}\ln\left(\frac{1+\frac{\lambda^{1/2}\cos\theta_0}{(1-\lambda)^{1/2}\sin\theta_0}}{1-\frac{\lambda^{1/2}\cos\theta_0}{(1-\lambda)^{1/2}\sin\theta_0}}\right)\right\} \tag{34}$$

and

$$\Phi(H) = \pi S\left(1-\frac{\cos\theta_0}{(1-\lambda)^{1/2}}\right). \tag{35}$$

Eq. (33) can be also deduced from Eqs. (14), (16), (17) and (18) for the special case $\phi_0 = 0$. It is interesting to note that Eqs. (34) and (35) agree exactly with the previous result (Eqs. (3.10) and (3.11) in Ref. 7) found by Garg for the molecular Fe_8 magnet.

II. $\pi/2 \geqslant \theta_H > 0$

For $\pi/2 \geqslant \theta_H > 0$, it is difficult to integrate the equation of motion Eq. (26). So we have to take the asymptotic form of zero-mode ($d\phi/d\tau$). Notice that $\phi \to \pi - \phi_0$ as $\tau \to +\infty$, we can expand $\mathrm{Im}\, f(\phi)$ according to the small parameter $\alpha = \phi - (\pi - \phi_0)$. Up to the leading term, Eq. (26) has the form

$$\dot{\phi} = -\omega_0\left(\phi - (\pi - \phi_0)\right), \tag{36}$$

where $\omega_0 = \frac{2K_1}{S}\lambda^{1/2}\sin\theta_0\cos\phi_0$. We then integrate the Eq. (36)

$$\phi = \pi - \phi_0 - c_0 e^{-\omega_0\tau}, \tag{37}$$

where c_0 is an integration constant. Therefore, the asymptotic form of zero-mode ($d\phi/d\tau$) can be written as

$$d\phi/d\tau = c_0\omega_0 e^{-\omega_0\tau}. \tag{38}$$

Straightforward, following Ref. 10, the tunnel splitting $\hbar\Delta^A$ and $\hbar\Delta^B$ corresponding to path A and B have the form

$$\hbar\Delta^A = c_A\omega_0^{3/2}\left(\frac{S^2}{2\pi K_1}\right)^{1/2}\left(\frac{\sin^2\theta_0}{\sin^2\theta_0+\lambda\cos^2\theta_0\sin^2\phi_0}\right)^{1/2} e^{-\operatorname{Re}(S_{cl}^A)}e^{-i\operatorname{Im}(S_{cl}^A)} \tag{39}$$

$$\hbar\Delta^B = c_B\omega_0^{3/2}\left(\frac{S^2}{2\pi K_1}\right)^{1/2}\left(\frac{\sin^2\theta_0}{\sin^2\theta_0+\lambda\cos^2\theta_0\sin^2\phi_0}\right)^{1/2} e^{-\operatorname{Re}(S_{cl}^B)}e^{-i\operatorname{Im}(S_{cl}^B)}, \tag{40}$$

where c_A and c_B are the numerical factors in order of $O(1)$ that come from the integration constant mentioned above (c_0 in Eq. (38)). Because the existence of H_y breaks the symmetry between the classical path A and B, c_A may not be equal to c_B. But for the small magnetic field, we assume theirs equivalence. Comparing Eqs. (39) and (40) with Eq. (33), we find

$$c_A = c_B = c\frac{4\sin\theta_0}{(1-\cos^2\theta_0-\lambda)^{1/2}}. \tag{41}$$

Now we turn to derive the total tunnel splitting $\hbar\Delta$ using a recently proposed effective Hamiltonian approach. For the present case, the effective Hamiltonian is found to be

$$\mathcal{H}_{eff} = \begin{bmatrix} 0 & \left(\hbar\Delta^A+\hbar\Delta^B\right) \\ \left(\hbar\Delta^A+\hbar\Delta^B\right)^* & 0 \end{bmatrix}. \tag{42}$$

Diagonalizing the effective Hamiltonian, we obtain the desired result as shown in Eqs. (18) and (19).

REFERENCES

[1] For an overview, see e.g., *Quantum Tunneling of Magnetization - QTM'94*, edited by L. Gunther and B. Barbara (Kluwer, Dordrecht, The Netherlands, 1994), and references therein.

[2] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature **365**, 141 (1993).

D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, Science **265**, 1054 (1994).

L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, Nature **383**, 145 (1996).

J. M. Hernandez, X. X. Zhang, F. Luis, J. Tejada, J. R. Friedman, M. P. Sarachik, and R. Ziolo, Phys. Rev. B **55**, 5858 (1997).

D. A. Garanin and E. M. Chudnovsky, Phys. Rev. B **56**, 11102(1997).

[3] A. -L. Barra, P. Debrunner, A. Catteschi, C. E. Schulz, and R. Sessoli, Europhys. Lett. **35**, 133 (1996).

C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett. **78**, 4645 (1997).

[4] D. Loss, D. P. Divicenzo, and G. Grinstein, Phys. Rev. Lett. **69**, 3232 (1992).

[5] J. V. Delft and G. L. Henley, Phys. Rev. Lett. **69**, 3236 (1992).

[6] A. Garg, Europhys. Lett. **22**, 205 (1993).

[7] A. Garg, Phys. Rev. B **60**, 6705 (1999).

[8] H. B. Braun and D. Loss, Europhys. Lett. **31**, 555 (1995).

[9] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999).

[10] A. Garg and G. -H. Kim, Phys. Rev. B **45**, 12921 (1992).

	$\theta_H = 0^o$		$\theta_H = 15^o$		$\theta_H = 30^o$		$\theta_H = 90^o$	
	Δ_d	Δ_i	Δ_d	Δ_i	Δ_d	Δ_i	Δ_d	Δ_i
$H_S = 0.0$T	0.00683	0.00683	0.00683	0.00683	0.00683	0.00683	0.00683	0.00683
$H_S = 0.2$T	0.00556	0.00558	0.00778	0.00780	0.01445	0.01448	0.05651	0.05658
$H_S = 0.4$T	0.00165	0.00167	0.01714	0.01733	0.06521	0.06591	0.75350	0.75752
$H_S = 0.6$T	0.00502	0.00515	0.04658	0.04782	0.29419	0.30232	8.20514	8.30553
$H_S = 0.8$T	0.01417	0.01485	0.13101	0.13783	1.34388	1.42229	73.1429	74.7913
$H_S = 1.0$T	0.02362	0.02548	0.39753	0.43399	6.19230	6.88449	537.366	557.203
$H_S = 1.2$T	0.02505	0.02808	1.31263	1.51459	28.5282	34.3140	3277.23	3462.35
$H_S = 1.4$T	0.00799	0.00942	4.70886	5.90363	129.907	176.358	16704.7	18092.3

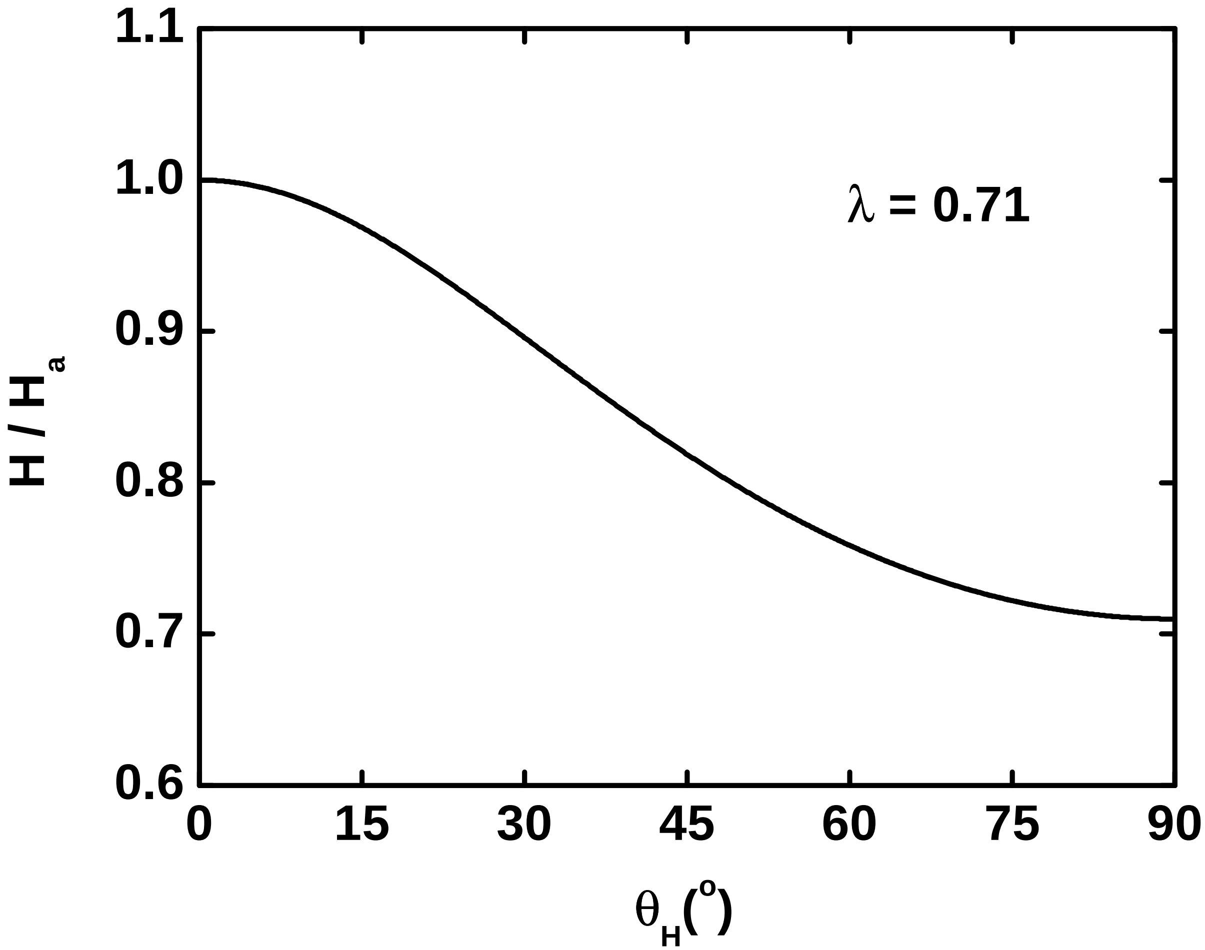
Table 1. The ground-state tunnel splitting Δ_d (calculated by diagonalization) and Δ_i (calculated by instanton approach) with $\theta_H = 0^o$, 15^o, 30^o and 90^o are listed as a function of magnetic field H_S. The units for the tunnel splitting and magnetic field are 10^{-7} Kelvin and Tesla, respectively. Here, $S = 10$, $K_1 = 32.1$K, $K_2 = 22.9$K and $\lambda = 0.71$ are used for the molecular Fe_8 magnet.

Figures Captions

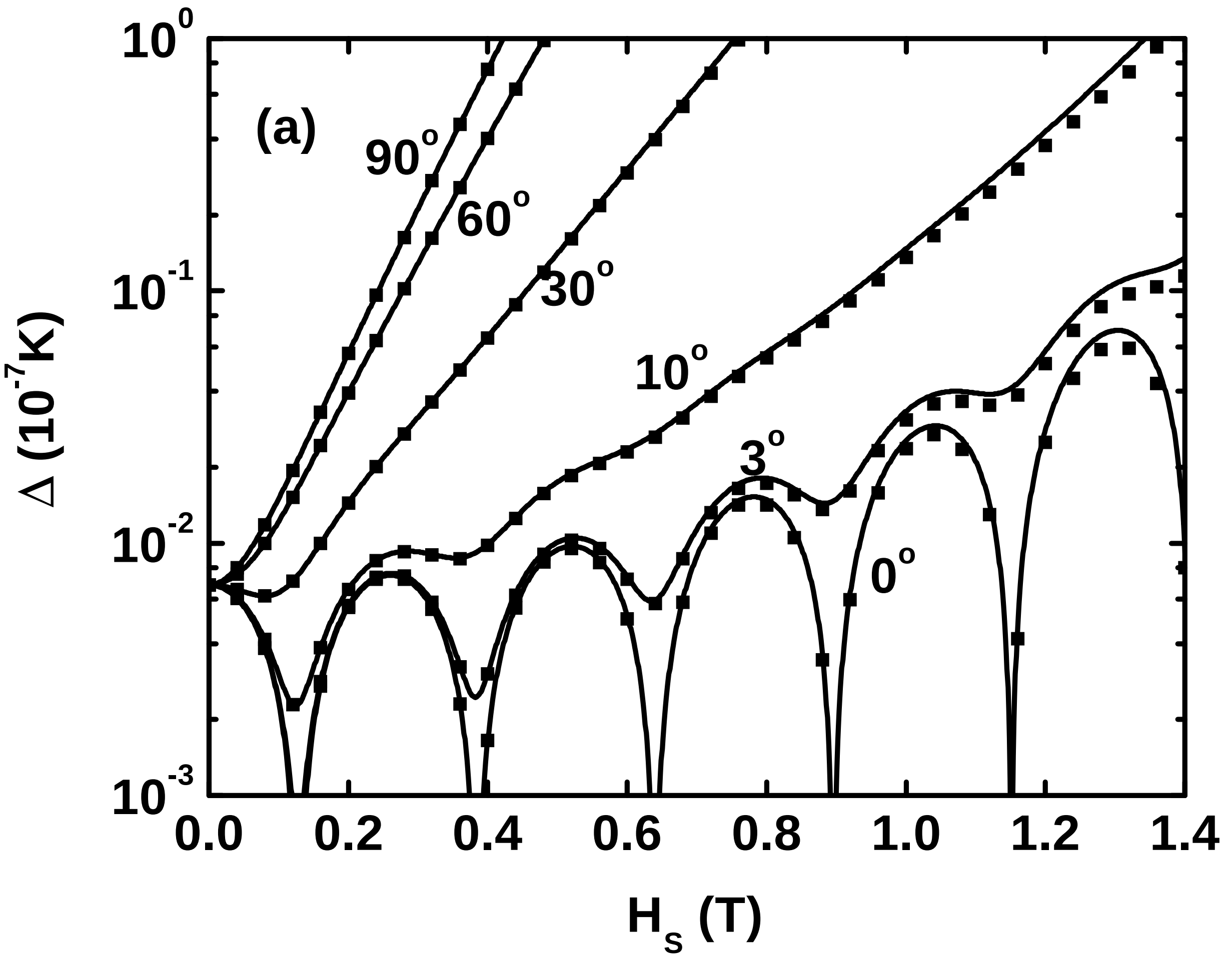
Fig. 1. The critical magnetic field H_c is plotted as a function of anlge θ_H at $\lambda = 0.71$.

Fig. 2. The ground-state tunnel splitting Δ are plotted as a function of the magnetic field H_S at $\theta_H = 0^o$, 3^o, 10^o, 30^o, 60^o, and 90^o for (a) $S = 10$ and (b) $S = 9.5$. The other parameters are $K_1 = 32.1$K, $K_2 = 22.9$K and $\lambda = 0.71$, the typical values of the molecular Fe_8 magnet. The results of the instanton approach and the exact diagonalization are represented by the solid lines and square symbols, respectively.

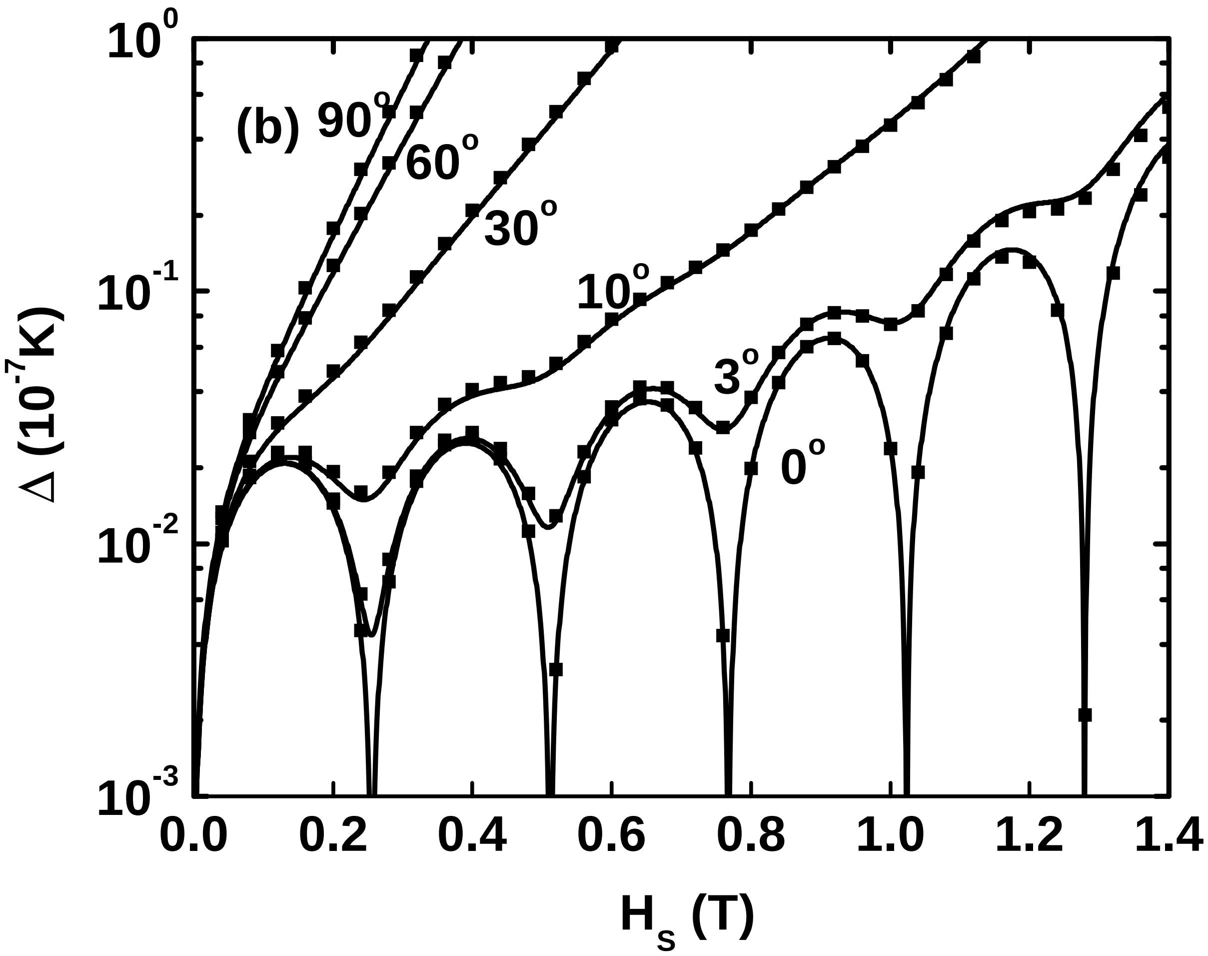
Fig. 3. The ground-state tunnel splitting Δ are plotted as a function of the magnetic field H_S for $\lambda = 0.3$, 0.5 and 0.7 with $S = 10$, $K_1 = 32.1$K at (a) $\theta_H = 0^o$ and (b) $\theta_H = 90^o$. The results of the instanton approach and the exact diagonalization are represented by the solid lines and square symbols, respectively.



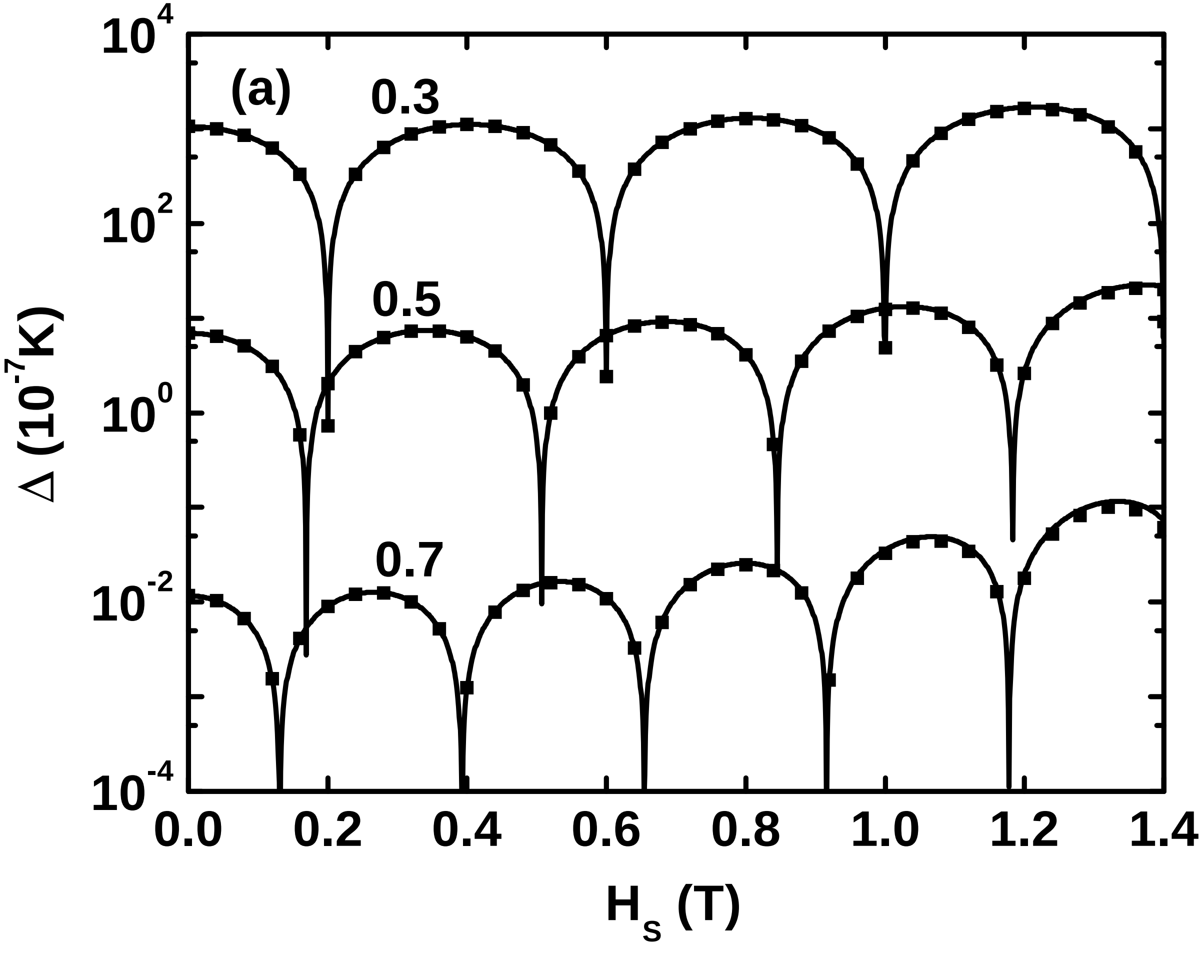
1.1
1.0
0.9
0.8
0.7
0.6
H / H_a
λ = 0.71
0
15
30
45
60
75
90
θ_H(°)



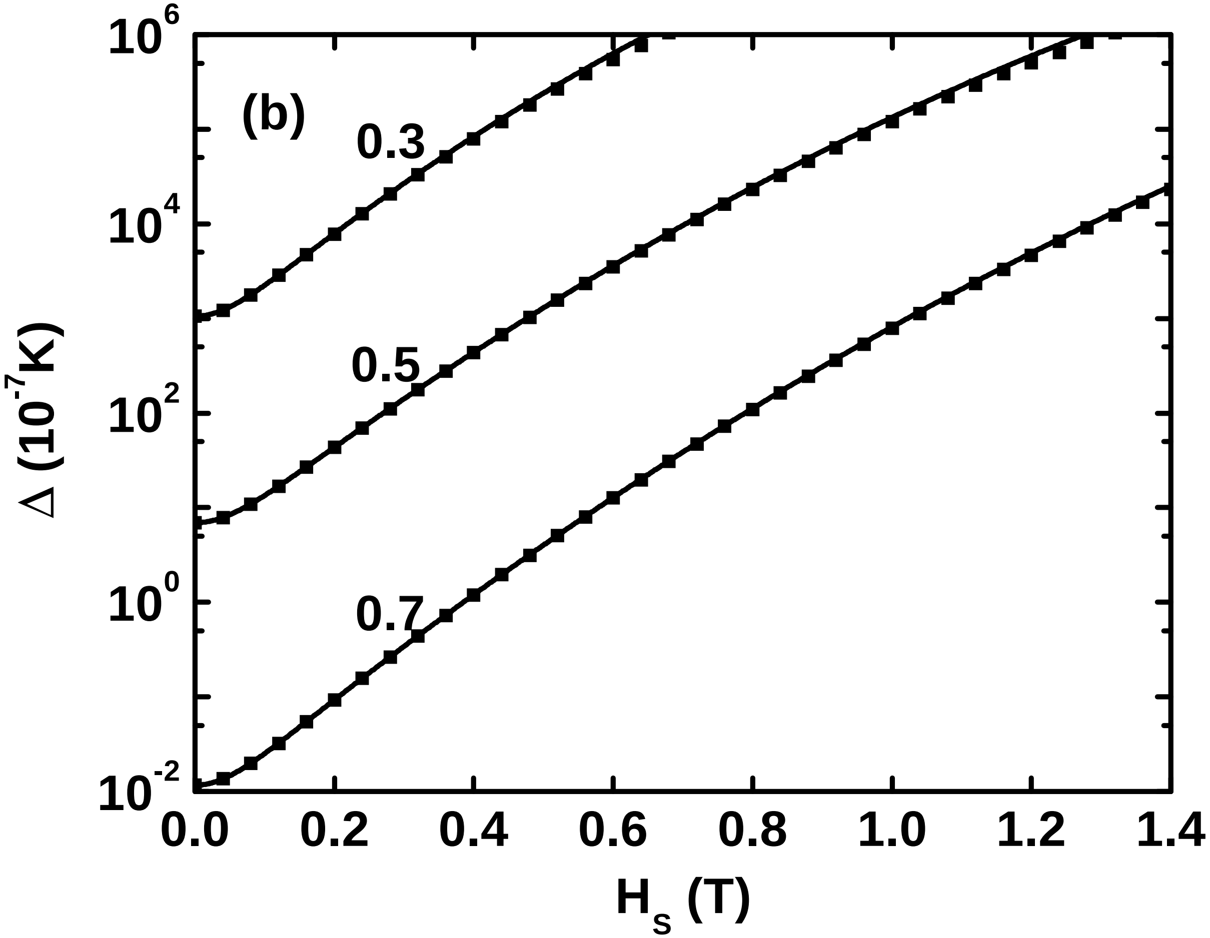
(a)
90°
60°
30°
10°
3°
0°
10^0
10^{-1}
10^{-2}
10^{-3}
Δ (10^{-7}K)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
H_S (T)



(b)
90°
60°
30°
10°
3°
0°
10^0
10^{-1}
10^{-2}
10^{-3}
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Δ (10^{-7}K)
H_S (T)



(a)
0.3
0.5
0.7
10^4
10^2
10^0
10^{-2}
10^{-4}
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Δ (10^{-7}K)
H_S (T)



(b)
0.3
0.5
0.7
10^6
10^4
10^2
10^0
10^{-2}
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
H_S (T)
Δ (10^{-7}K)